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(72) Sandstrom, Paul Harry, US

(72) Wideman, Lawson Gibson, US

(71) GOODYEAR TIRE & RUBBER COMPANY (THE), US

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(54) **COMPOSITION CAOUTCHOUEUSE RENFORCEE DE  
SILICE; PNEU A BANDE A BASE DE CETTE COMPOSITION**  
(54) **SILICA REINFORCED RUBBER COMPOSITION AND TIRE  
WITH TREAD THEREOF**

(57) Composition de caoutchouc contenant un renfort de silice, ainsi que des pneus dont les bandes de roulement sont fabriquées à partir de cette composition. Composition de caoutchouc comprenant au moins un élastomère, de la silice, du noir de carbone et un agent de couplage de la silice composé d'un mélange de 3,3'-tétrathiodipropanol polysulfure.

(57) The present invention relates to a rubber composition containing silica reinforcement and to pneumatic tires having treads comprised of such rubber composition. A rubber composition comprises at least one elastomer, silica, carbon black and a silica coupler comprised of 3,3'-tetrathiodipropanol polysulfide mixture.

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Abstract of the Disclosure

SILICA REINFORCED RUBBER COMPOSITION  
AND TIRE WITH TREAD THEREOF

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The present invention relates to a rubber composition containing silica reinforcement and to pneumatic tires having treads comprised of such rubber composition.

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A rubber composition comprises at least one elastomer, silica, carbon black and a silica coupler comprised of 3,3'-tetrathiodipropanol polysulfide mixture.

SILICA REINFORCED RUBBER COMPOSITION  
AND TIRE WITH TREAD THEREOF

Field

5        This invention relates to rubber compositions  
which contain silica reinforcement and to tires having  
treads thereof. In one aspect, the rubber composition  
is comprised of rubber, particularly sulfur cured  
10       rubber, reinforced with a combination of silica, and  
optionally carbon black, and a 3,3'-  
tetrathiodipropanol polysulfide mixture coupling  
agent.

Background

15       For various applications utilizing rubber which  
requires high strength and abrasion resistance,  
particularly applications such as tires and various  
industrial products, sulfur cured rubber is utilized  
which contains substantial amounts of reinforcing  
20       fillers, often in a range of about 35 to about 85  
parts by weight per 100 parts rubber. Carbon black is  
commonly used for such purpose and normally provides  
or enhances good physical properties for the sulfur  
cured rubber. Particulate silica is also often used  
25       for such purpose, particularly when the silica is used  
in conjunction with a coupling agent. In some cases,  
a combination of silica and carbon black is utilized  
for reinforcing fillers for various rubber products,  
including treads for tires. The use of such  
30       reinforcing fillers for elastomers, including sulfur  
curable elastomers, is well known to those skilled in  
such art.

      It is important to appreciate that,  
conventionally, carbon black is a considerably more  
35       effective reinforcing filler for rubber products, and  
particularly for rubber tire treads than silica if the

silica is used without a coupling agent, or silica coupler or silica adhesion agent as it may be sometimes referred to herein.

Such coupling agents may, for example, be  
5 premixed, or pre-reacted, with the silica particles or added to the rubber mix during a rubber/silica processing, or mixing, stage. If the coupling agent and silica are added separately to the rubber mix during the rubber/silica mixing, or processing stage,  
10 it is considered that the coupling agent then combines in situ with the silica.

In particular, such coupling agents are sometimes composed of a silane which has a constituent component, or moiety, (the silane portion) capable of  
15 reacting with the silica surface and, also, a constituent component, or moiety, capable of reacting with the rubber, particularly a sulfur vulcanizable rubber which contains carbon-to-carbon double bonds, or unsaturation. In this manner, then the coupler  
20 acts as a connecting bridge between the silica and the rubber and thereby enhances the rubber reinforcement aspect of the silica.

In one aspect, the silane of the coupling agent apparently forms a bond to the silica surface and the  
25 rubber reactive component of the coupling agent combines with the rubber itself. Usually the rubber reactive component of the coupler is temperature sensitive and tends to combine with the rubber during the final and higher temperature sulfur vulcanization stage and, thus, subsequent to the rubber/silica/  
30 coupler mixing stage and, therefore, after the silane group of the coupler has combined with the silica. However, partly because of typical temperature sensitivity of the coupler, some degree of  
35 combination, or bonding, may occur between the rubber-reactive component of the coupler and the rubber

during initial rubber/silica/coupler mixing stage(s) and, thus, prior to a subsequent vulcanization stage.

The rubber-reactive group component of the coupler may be, for example, one or more of groups  
5 such as mercapto, amino, vinyl, epoxy, and sulfur groups, and is often a sulfur or mercapto moiety and more usually sulfur.

Numerous coupling agents are taught for use in combining silica and rubber, such as, for example,  
10 silane coupling agents containing a polysulfide component, or structure, such as, for example, trialkoxyorganosilane polysulfides containing from 2 to 8 sulfur atoms in a polysulfide bridge such as, for example, bis-(3-triethoxysilylpropyl)tetrasulfide  
15 and/or trisulfide.

Various U.S. patents relating to silicas and silica reinforced tire treads include, for example, U.S. Patents Nos. 3,451,458; 3,664,403; 3,768,537; 3,884,285; 3,938,574; 4,482,663; 4,590,052; 5,089,554  
20 and British 1,424,503.

Various hydroxysulfides have also been used to reinforce silica in carbon black filled rubber (EP Patent Publication No. 489,313).

The term "phr" if used herein, and according to  
25 conventional practice, refers to "parts of a respective material per 100 parts by weight of rubber, or elastomer".

In the description of this invention, the terms "rubber" and "elastomer" if used herein, may be used  
30 interchangeably, unless otherwise prescribed. The terms "rubber composition", "compounded rubber" and "rubber compound", if used herein, are used interchangeably to refer to "rubber which has been blended or mixed with various ingredients and  
35 materials" and such terms are well known to those

having skill in the rubber mixing or rubber compounding art.

A reference to an elastomer's T<sub>g</sub> refers to its glass transition temperature, which can conveniently be determined by a differential scanning calorimeter at a heating rate of 10°C per minute.

#### Summary and Practice of the Invention

In accordance with one aspect of this invention, a rubber composition is provided which comprises (A) 100 parts by weight of at least one diene-based elastomer, (B) about 25 to about 100, optionally about 35 to about 90, phr of filler composed of silica and carbon black, and (C) a silica coupler selected from (i) 3,3'-tetrathiodipropanol polysulfide mixture or (ii) a combination of about 95 to about 25, alternatively about 90 to about 55, weight percent 3,3'-tetrathiodipropanol polysulfide mixture containing 1 to 8 atoms in the polysulfide bridge and, correspondingly, about 5 to about 75, alternatively about 10 to about 45, weight percent of bis-(3-trialkoxysilylalkyl) polysulfide containing from 2 to 8 sulfur atoms in the polysulfide bridge such as, for example, at least one of bis-(3-triethoxysilylpropyl)tetrasulfide and bis-(3-triethoxysilylpropyl)trisulfide; wherein the weight ratio of silica to carbon black is at least 0.1/1, optionally at least 3/1 and optionally at least 10/1.

Typically, it is desired that the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1.

In one aspect of the invention, such a rubber composition is provided which is comprised of (A) 100 parts by weight of at least one diene-based elastomer, (B) about 25 to about 90 phr particulate silica, (C) up to about 30 phr carbon black, and (D) a silica

coupler which is collectively composed of about 90 to about 55 weight percent 3,3'-tetrathiodipropanol, about 10 to about 45 weight percent of at least one of bis-(3-triethoxysilylpropyl)tetrasulfide and bis-(3-  
5 triethoxysilylpropyl)trisulfide wherein the weight ratio of silica to carbon black is in a range of about 3/1 to about 30/1; wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters per gram and a  
10 dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

Typically, it is desired that the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1.

15 Thus, in one aspect of the invention, the rubber composition contains a combination of both silica and carbon black as elastomer reinforcing pigments.

The rubber composition may contain a minor amount of silica in its silica/carbon black or it may be  
20 quantitatively reinforced with silica where carbon black is present in a minor amount.

In another aspect of the invention, a tire is provided having a tread comprised of the said rubber composition of this invention.

25 The 3,3'-tetrathiodipropanol polysulfide mixture may more fully be described as a highly polar difunctional alcohol that can strongly associate to the silica and further react with a diene polymer through its polysulfide bridge which contains 1 to 8  
30 sulfur atoms.

The 3,3'-tetrathiodipropanol polysulfide is referred to herein as a mixture because all of the possible sulfide bridges with 1 to 8 sulfur atoms are present.

35 It is believed that the 3,3'-tetrathiodipropanol polysulfide mixture, with its alcohol

moiety/associated with the surface of the silica, acts to pull the silica filler closer to the diene rubber and, thus, give much better dispersion of the silica into the rubber compound, apparently by somewhat  
5 inhibiting, or retarding, the tendency of the silica particles to agglomerate together. This is considered herein to be beneficial because the better the silica dispersion within the rubber (eg: less silica agglomeration) is expected to provide better physical  
10 properties to the rubber.

In practice, preferably the 3,3'-tetrathiodipropanol polysulfide mixture is reacted, or caused to be associated, with the silica in situ by mixing it and the silica together with the rubber  
15 composition instead of pre-reacting them before adding to the rubber composition.

Where it is desired that the rubber composition is primarily reinforced with silica as the reinforcing pigment, it is preferable that the weight ratio of  
20 silica to carbon black is at least 3/1, preferably at least 10/1 and, thus, for example, in a range of about 3/1 to about 30/1.

In one aspect of the invention, the silica coupler consists essentially of the 3,3'-  
25 tetrathiodipropanol polysulfide mixture.

In a further aspect, the silica coupler can be composed of a combination of the 3,3'-tetrathiodipropanol polysulfide mixture together with bis-(3-triethoxysilylpropyl)tetrasulfide and/or a  
30 blend of such tetrasulfide and bis-(3-triethoxysilylpropyl)trisulfide.

The 3,3'-tetrathiodipropanol can also be referred to as an associative alcohol coupler. In one aspect, it can also be referred to as a non-silane silica-to-  
35 rubber coupler. In particular, it can be characterized by having the properties of being a



highly viscous liquid with an infrared spectrometric absorption bond of medium intensity in a range of about  $3570\text{cm}^{-1}$  to about  $3450\text{cm}^{-1}$  for the alcohol functional group.

5           Field desorption and gas chromatographic mass spectrometry analysis indicated that the 3-3'-tetrathiodipropanol polysulfide has 1 to 8 sulfur atoms in the polysulfide bridge.

10           The 3,3'-tetrathiodipropanol polysulfidic mixture is considered herein to be particularly advantageous for the practice of this invention because it has a very strong associative attraction to silica and high reactivity for diene rubber which is considered to be a benefit to the exceptionally good dispersion of  
15           silica into the rubber.

Historically, the more homogeneous the dispersion of rubber compound components into the rubber, the better the resultant cured properties of that rubber. The 3,3'-tetrathiodipropanol's strong association to  
20           silica and high affinity, compatibility, and reactivity with rubber is considered herein to lead to excellent silica dispersion.

In one aspect, such a rubber composition can be provided as being sulfur cured. The sulfur curing is  
25           accomplished in a conventional manner, namely, by curing under conditions of elevated temperature and pressure for a suitable period of time.

In the practice of this invention, as hereinbefore pointed out, the rubber composition is  
30           comprised of at least one diene-based elastomer, or rubber. Thus, it is considered that the elastomer is a sulfur curable elastomer. Such elastomer, or rubber, may be selected, for example, from at least one of cis 1,4-polyisoprene rubber (natural and/or  
35           synthetic, and preferably natural rubber), 3,4-polyisoprene rubber, styrene/butadiene copolymer

rubbers, styrene/isoprene/butadiene terpolymer rubbers, and cis 1,4-polybutadiene rubber.

In one aspect the rubber is preferably of at least two diene based rubbers. Such diene based  
5 rubbers may, for example, be of homopolymers and copolymers of conjugated diene hydrocarbons and copolymers of at least one diene hydrocarbon with a vinyl aromatic compound. Such diene hydrocarbons may be, for example, selected from 1,3-butadiene and  
10 isoprene. Such vinyl aromatic compound may be, for example, styrene or alphas-methylstyrene. For example, a combination of two or more rubbers is preferred such as at least elastomers selected from cis 1,4-polyisoprene rubber (natural or synthetic, although  
15 natural is preferred), 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene rubber, emulsion and solution polymerization derived styrene/butadiene rubbers, cis 1,4-polybutadiene rubber, medium vinyl polybutadiene rubber having a  
20 vinyl content of from 30 to 50, high vinyl polybutadiene having a vinyl content of from 50 to 75, and emulsion polymerization prepared butadiene/acrylonitrile copolymers.

In one aspect of this invention, an emulsion  
25 polymerization derived styrene/butadiene (E-SBR) might be used having a relatively conventional styrene content of about 20 to about 28 percent bound styrene or, for some applications, an E-SBR having a medium to relatively high bound styrene content, namely, a bound  
30 styrene content of about 30 to about 45 percent.

The relatively high styrene content of about 30 to about 45 for the E-SBR can be considered beneficial for a purpose of enhancing traction, or skid resistance, of the tire tread. The presence of the E-SBR itself is considered beneficial for a purpose of  
35 enhancing processability of the uncured elastomer

composition mixture, especially in comparison to a utilization of a solution polymerization prepared SBR (S-SBR).

5 By emulsion polymerization prepared E-SBR, it is meant that styrene and 1,3-butadiene are copolymerized as an aqueous emulsion. Such are well known to those skilled in such art. The bound styrene content can vary, for example, from about 5 to 50%. In one aspect, the E-SBR may also contain acrylonitrile to  
10 form a terpolymer rubber, as E-SBAR, in amounts, for example, of about 2 to about 30 weight percent bound acrylonitrile in the terpolymer.

Emulsion polymerization prepared styrene/butadiene/acrylonitrile copolymer rubbers  
15 containing about 2 to about 40 weight percent bound acrylonitrile in the copolymer are also contemplated as diene based rubbers for use in this invention.

The solution polymerization prepared SBR (S-SBR) typically has a bound styrene content in a range of  
20 about 5 to about 50, preferably about 9 to about 36, percent. The S-SBR can be conveniently prepared, for example, by organo lithium catalyzation in the presence of an organic hydrocarbon solvent.

A purpose of using S-SBR is for improved tire  
25 rolling resistance as a result of lower hysteresis when it is used in a tire tread composition.

The 3,4-polyisoprene rubber (3,4-PI) is considered beneficial for a purpose of enhancing the tire's traction when it is used in a tire tread  
30 composition.

The 3,4-PI and use thereof is more fully described in U.S. Patent No. 5,087,668 which is incorporated herein by reference. The T<sub>g</sub> refers to the glass transition temperature which can  
35 conveniently be determined by a differential scanning calorimeter at a heating rate of 10°C per minute.

The cis 1,4-polybutadiene rubber (BR) is considered to be beneficial for a purpose of enhancing the tire tread's wear, or treadwear.

Such BR can be prepared, for example, by organic  
5 solution polymerization of 1,3-butadiene.

The BR may be conveniently characterized, for example, by having at least a 90% cis 1,4-content.

The cis 1,4-polyisoprene and cis 1,4-polyisoprene natural rubber are well known to those having skill in  
10 the rubber art.

The vulcanized rubber composition should contain a sufficient amount of silica, and carbon black reinforcing filler(s) to contribute a reasonably high modulus and high resistance to tear. The combined  
15 weight of the silica and carbon black, as hereinbefore referenced, may be as low as about 30 parts per 100 parts rubber, but is preferably from about 35 or 45 to about 90 parts by weight.

The commonly employed siliceous pigments used in  
20 rubber compounding applications can be used as the silica in this invention, including pyrogenic and precipitated siliceous pigments (silica), although precipitate silicas are preferred.

The siliceous pigments preferably employed in  
25 this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate.

Such silicas might be characterized, for example, by having a BET surface area, as measured using  
30 nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, page 304  
35 (1930).

The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300.

5       The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

10       Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc;  
15       silicas available from Rhone-Poulenc, with, for example, Zeosil 1165MP and silicas available from Degussa AG with, for example, designations VN2 and VN3, etc.

20       It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, curing  
25       aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing  
30       agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and  
35       commonly used in conventional amounts.

Typical amounts of reinforcing type carbon blacks(s), for this invention, if used, are hereinbefore set forth. It is to be appreciated that the silica coupler may be used in conjunction with a carbon black, namely, pre-mixed with a carbon black prior to addition to the rubber composition, and such carbon black is to be included in the aforesaid amount of carbon black for the rubber composition formulation. Typical amounts of tackifier resins, if used, comprise about 0.5 to about 10 phr, usually about 1 to about 5 phr. Typical amounts of processing aids comprise about 1 to about 50 phr. Such processing aids can include, for example, aromatic, naphthenic, and/or paraffinic processing oils. Typical amounts of antioxidants comprise about 1 to about 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in the Vanderbilt Rubber Handbook (1978), pages 344-346. Typical amounts of antiozonants comprise about 1 to 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise about 0.5 to about 3 phr. Typical amounts of zinc oxide comprise about 2 to about 5 phr. Typical amounts of waxes comprise about 1 to about 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise about 0.1 to about 1 phr. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide.

The vulcanization is conducted in the presence of a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to

those skilled in the art, sulfur vulcanizing agents are used in an amount ranging from about 0.5 to about 4 phr, or even, in some circumstances, up to about 8 phr, with a range of from about 1.5 to about 2.5, sometimes from 2 to 2.5, being preferred.

Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally and preferably, a primary accelerator(s) is used in total amounts ranging from about 0.5 to about 4, preferably about 0.8 to about 1.5, phr. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in smaller amounts (of about 0.05 to about 3 phr) in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators might be expected to produce a synergistic effect on the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound. The presence and relative amounts of sulfur vulcanizing agent and accelerator(s) are not considered to be an aspect of this invention which is more primarily directed to the

use of silica as a reinforcing filler in combination with 3,3'-tetrathiodipropanol polysulfide mixture as a coupling agent for the reinforcing filler.

5       The presence and relative amounts of the above additives are not considered to be an aspect of the present invention which is more primarily directed to the utilization of specified blends of rubbers in rubber compositions, in combination with silica and with 3,3'-tetrathiodipropanol polysulfide mixture  
10 individually or in combination with bis-(3-triethoxysilylpropyl)tetrasulfide (a polysulfide mixture) as well as, optionally, carbon black, for the reinforcement of the rubber.

15       The mixing of the rubber composition can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages, namely, at least one non-productive stage followed by a productive mix stage. The final curatives are  
20 typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber, silica and silica coupler, and  
25 carbon black if used, are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art.

30       The rubber composition of this invention can be used for various purposes. For example, it can be used for various tire compounds. Such tires can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those  
35 having skill in such art.



The invention may be better understood by reference to the following examples in which the parts and percentages are by weight unless otherwise indicated.

5

EXAMPLE I

In this Example, 3,3'-tetrathiodipropanol polysulfide mixture on a carbon black carrier was  
10 evaluated as an alternative for a relatively commonly used silica coupling agent, namely, bis-(3-triethoxysilylpropyl)tetrasulfide polysulfide mixture, on a carbon black as a carrier, in a silica reinforced rubber composition.

15 The rubber compositions containing the materials set out in Table 1 were prepared in a BR Banbury rubber mixer using three separate, sequential stages of addition (mixing), namely, two non-productive mix stages and one final productive mix to temperatures of  
20 160°C, 160°C and 120°C and times of 4 minutes, 4 minutes and 2 minutes, respectively. The amount of coupler is listed as being "variable" in Table 1 and is more specifically set forth in Table 2.

It is clearly evident that utilization of the  
25 coupling agent appears to be necessary to obtain suitable cured properties in a silica containing rubber composition, or compound. Such properties include tensile strength at break, the 100 and 300% modulus values, rebound hardness, Rheovibron E' and  
30 particularly DIN abrasion resistance (lower indicate less, or values better, abrasion values). Samples 2 and 3, when compared to Sample 1, which was prepared in the absence of utilization of the silica coupling agent, clearly show the advantage of the coupling  
35 agents. The properties of Sample 3, which contains the silica coupler utilized in this invention has

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properties comparable to those exhibited by Sample 2 which contains the conventional silane coupling agent.

In particular, this Example shows that the 3,3'-tetrathiodipropanol polysulfide mixture, as utilized in Sample 3, can provide significant improvements in modulus, rebound, hardness and abrasion when compared to control Sample 1 which does not contain coupling agent. Furthermore, these properties compare favorably to those of Sample 2 which contains the conventional silane coupling agent.

Table 1	
<u>1st Non-Productive</u>	
Natural Rubber <sup>1</sup>	100.00
Carbon Black	35.00
Processing Oil	5.00
Zinc Oxide	5.00
Fatty Acid	2.00
Antioxidant <sup>2</sup>	2.00
<u>2nd Non-Productive</u>	
Silica <sup>3</sup>	15.00
Bis-(3-triethoxysilylpropyl) tetrasulfide <sup>4</sup>	variable
3,3'-tetrathiodipropanol polysulfide mixture	variable
<u>Productive</u>	
Sulfur	1.40
Accelerator, sulfenamide type	1.00

- 1) Synthetic cis 1,4-polyisoprene rubber (NAT 2200) from The Goodyear Tire & Rubber Company;

- 2) of the polymerized 1,2-dihydro-2,2,4-trimethylquinoline type;
- 3) silica obtained as Hi-Sil-210 from PPG Industries, Inc.;
- 4) 50% active composite composed of the organosilane tetrasulfide on or with carbon black in a 50/50 weight ratio available as material X50S from Degussa GmbH.  
Technically the organosilane polysulfide is understood to be a composite, or mixture, in which the average polysulfide bridge contains about 3.5 to 4 connecting sulfur atoms, although the mixture may contain such polysulfides with about 2 to 8 connecting sulfur atoms.
- 5) 3,3'-tetrathiodipropanol polysulfide containing 1 to 8 sulfur atoms in the polysulfide bridge obtained as a highly viscous liquid from the reaction of 3-chloropropanol (two molar equivalents) with 1 molar equivalent of aqueous sodium tetrasulfide. It is supported 1 to 1 by weight on N330 carbon black for all examples used in this specification.

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Table 2			
Sample #	1	2	3
X50S (Degussa GmbH)	0	3	0
3,3'-tetrathiodipropanol	0	0	2
Rheometer (150°C)			
Max. Torque, dNm	30.2	34.3	33.0
Min. Torque, dNm	7.0	7.0	7.0
Delta Torque	23.2	27.3	26.0
T <sub>90</sub> , minutes	23.0	18.7	17.0
Stress-Strain			
Tensile Strength, MPa	17.6	19.7	18.8
Elongation at Break, %	630	621	626
100% Modulus, MPa	1.2	1.7	1.5
300% Modulus, MPa	5.5	8.0	6.8
Rebound			
100°C, %	55.1	59.8	58.6
Hardness			
Shore A, 100°C	46.4	51.9	51.2
Rheovibron			
E' at 60°C, MPa	10.6	11.5	10.4
Tan Delta at 60%	.105	.092	.097
DIN Abrasion	231	156	186

#### EXAMPLE II

In this Example, 3,3'-tetrathiodipropanol polysulfide mixture on a carbon black carrier was evaluated as a silica coupling agent in a silica reinforced rubber composition.

The rubber compositions containing the materials set out in Table 3 were prepared in a BR Banbury rubber mixer using three separate, sequential stages of addition (mixing), namely, two non-productive mix

stages and one final productive mix to temperatures of 160°C, 160°C and 120°C and times of 4 minutes, 4 minutes and 2 minutes, respectively. The amount of coupler is listed in Table 3 and is more specifically set forth in Table 4.

It is clearly evident that utilization of the coupling agent appears to be necessary to obtain suitable cured properties in a silica containing rubber composition, or compound. Such properties include tensile strength at break, the 100 and 300% modulus values, rebound hardness, Rheovibron E' and particularly DIN abrasion resistance (lower indicate less, or values better, abrasion values). Sample 5 of Table 4, when compared to Sample 4 of Table 4, which was prepared in the absence of utilization of the silica coupling agent, clearly show the advantage of the coupling agent. This Example shows that the 3,3'-tetrathiodipropanol polysulfide mixture, as utilized in Sample 5, can provide improvements in modulus, rebound, hardness and abrasion when compared to control Sample 4 which does not contain coupling agent.

Table 3	
<u>1st Non-Productive</u>	
Natural Rubber <sup>1</sup>	100.00
Silica <sup>2</sup>	20.00
Carbon Black	15.00
Processing Oil	5.00
Zinc Oxide	5.00
Fatty Acid	2.00
Antioxidant <sup>3</sup>	2.00
3,3'-tetrathiodipropanol polysulfide mixture <sup>4</sup>	0 or 3.00
<u>2nd Non-Productive</u>	
Silica <sup>2</sup>	15.00
<u>Productive</u>	
Sulfur	2.00
Accelerators, sulfenamide type	2.50
Diphenyl guanidine	1.00

- 1) Synthetic cis 1,4-polyisoprene rubber (NAT 2200) from The Goodyear Tire & Rubber Company;
- 2) silica obtained as Hi-Sil-210 from PPG Industries, Inc.;
- 3) of the polymerized 1,2-dihydro-2,2,4-trimethylquinoline type;
- 4) 3,3'-tetrathiodipropanol polysulfide containing 1 to 8 sulfur atoms in the polysulfide bridge obtained as a highly viscous liquid from the reaction of 3-chloropropanol (two molar equivalents) with 1 molar equivalent of aqueous sodium tetrasulfide. It is supported 1 to 1 by

weight on N330 carbon black for all examples used in this specification.

Table 4			
5	<u>Sample #</u>	<u>4</u>	<u>5</u>
	3,3'-tetrathiodipropanol mixture	0	3
<u>Rheometer (150°C)</u>			
10	Max. Torque, dNm	50.1	48.5
	Min. Torque, dNm	8.3	5.0
	Delta Torque	41.8	43.5
	T <sub>90</sub> , minutes	14.3	10.0
<u>Stress-Strain</u>			
15	Tensile Strength, MPa	18.4	19.2
	Elongation at Break, %	574	526
	100% Modulus, MPa	1.9	2.6
	300% Modulus, MPa	6.8	9.9
<u>Rebound</u>			
20	100°C, %	64.9	66.8
	<u>Hardness</u>		
	Shore A, 100°C	62.9	64.8
	<u>Rheovibron</u>		
25	E' at 60°C, MPa	19.1	20.0
	Tan Delta at 60%	.050	.054
	DIN Abrasion	193	180

### EXAMPLE III

In this Example, 3,3'-tetrathiodipropanol polysulfide mixture was evaluated as a coupling agent in a highly silica loaded rubber composition. Rubber compositions containing the materials set out in Table 5 were prepared in a BR Banbury mixer using three

separate, sequential stages of addition, namely, two non-productive mix stages and one productive mix stage to temperatures of 160°C, 160°C and 120°C and times of 4 minutes, 4 minutes and 2 minutes, respectively. The cure behavior and cured properties are indicated in Table 8.

The use of 3,3'-tetrathiodipropanol polysulfide alone or in combination with the conventional coupling agent gave rubber compositions exhibiting excellent cured properties in the presence of high levels of silica filler.

Table 5	
<i>1st Non-Productive</i>	
Styrene/Butadiene Rubber <sup>1</sup>	68.75
Polybutadiene Rubber <sup>2</sup>	15.00
Natural Rubber	35.00
Carbon Black <sup>3</sup>	20.00
Silica <sup>4</sup>	40.00
Zinc Oxide	3.00
Fatty Acid	3.00
Antioxidant <sup>5</sup>	2.00
Processing Aid <sup>6</sup>	5.00
3,3'-tetrathiodipropanol sulfide <sup>8</sup>	4.00
<i>2nd Non-Productive</i>	
Silica <sup>4</sup>	30.00
Bis-(3-triethoxysilylpropyl) tetrasulfide <sup>7</sup> (50% active)	0 or 3.00
3,3'-tetrathiodipropanol polysulfide <sup>8</sup>	0 or 3.00
<i>Productive</i>	
Sulfur	1.40
Accelerator, sulfenamide type	1.80
Diphenyl guanidine	1.50



- 1) Emulsion polymerization prepared  
styrene/butadiene copolymer elastomer  
containing 23.5% bound styrene and 37.5 phr  
aromatic oil from The Goodyear Tire & Rubber  
Company;  
5
- 2) high cis 1,4-polybutadiene from The Goodyear  
Tire & Rubber Company;
- 10 3) carbon black as N330;
- 4) Zeosil 1165 MP from Rhone-Poulenc;
- 5) polymerized 1,2-dihydro-2,2,4-  
trimethylquinoline type;  
15
- 6) Struktol A6;
- 7) 50% active composite composed of the  
organosilane tetrasulfide on or with carbon  
black in a 50/50 weight ratio available as  
material X50S from Degussa GmbH.  
20
- 8) 3,3'-tetrathiodipropanol polysulfide  
containing 1 to 8 sulfur atoms in the  
polysulfide bridge obtained as a highly  
viscous liquid from the reaction of 3-  
chloropropanol (two molar equivalents) with  
1 molar equivalent of aqueous sodium  
tetrasulfide. It is supported 1 to 1 by  
weight on N330 carbon black for all examples  
used in this specification.  
25  
30

Table 6		
<u>Sample #</u>	<u>6</u>	<u>7</u>
X50S (Degussa GmbH)	3.0	0
3,3'-tetrathiodipropanol	4.0	7.0
<u>Rheometer (150°C)</u>		
Max. Torque, dNm	45.0	41.4
Min. Torque, dNm	10.0	9.0
Delta Torque	35.0	32.5
T <sub>90</sub> , minutes	17.5	25.0
<u>Stress-Strain</u>		
Tensile Strength, MPa	13.0	11.9
Elongation at Break, %	474	548
100% Modulus, MPa	2.54	2.0
300% Modulus, MPa	8.75	6.14
<u>Rebound</u>		
100°C, %	52.5	46.9
<u>Hardness</u>		
Shore A, 100°C	59.9	55.3
<u>Rheovibron</u>		
E' at 60°C, MPa	37.6	35.0
Tan Delta at 60%	.086	.100
DIN Abrasion	147	161

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

WHAT IS CLAIMED IS:

1. A rubber composition comprised of (A) 100 parts by weight of at least one diene-based elastomer, (B) about 25 to about 100 phr of filler composed of particulate, precipitated silica and carbon black, and (C) a silica coupler selected from (i) 3,3'-tetrathiodipropanol polysulfide mixture containing 1 to 8 sulfur atoms in the polysulfidic bridge or from (ii) a combination of about 95 to about 25 weight percent 3,3'-tetrathiodipropanol polysulfide mixture and, correspondingly, about 5 to about 75 weight percent of bis-(3-trialkoxysilylalkyl) polysulfide containing from 2 to 8 sulfur atoms in its polysulfide bridge wherein the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1; wherein the weight ratio of silica to carbon black, is at least about 0.1/1.
2. The rubber composition of claim 1 wherein the said silica coupler consists essentially of 3,3'-tetrathiodipropanol polysulfide mixture; and wherein the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1
3. The rubber composition of claim 1 where the said 3,3'-tetrathiodipropanol polysulfide mixture is supported on carbon black carrier.
4. The rubber composition of claim 1 wherein the said silica coupler is a combination of about 95 to about 25 weight percent 3,3'-tetrathiodipropanol polysulfide mixture and, correspondingly, about 5 to about 75 weight percent of bis-(3-triethoxysilylpropyl)tetrasulfide and bis-(3-triethoxysilylpropyl)trisulfide.

5. The rubber composition of claim 1 wherein the diene based elastomer is selected from at least one of cis 1,4-polyisoprene rubber, 3,4-polyisoprene rubber, styrene/butadiene copolymer rubbers, 5 isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubbers, cis 1,4-polybutadiene rubber, medium vinyl polybutadiene rubber, high vinyl polybutadiene rubber and emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer 10 rubber and butadiene/acrylonitrile copolymer rubber.

6. The rubber composition of claim 1 wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters 15 per gram and a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

7. The rubber composition of claim 2 wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters 20 per gram and a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

8. The rubber composition of claim 3 wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters 25 per gram and a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

9. A rubber composition comprised of (A) 100 parts by weight of at least one diene-based elastomer, (B) about 25 to about 90 phr particulate silica, (C) up to about 30 phr carbon black, and (D) a silica coupler which is collectively composed of about 90 to 30 about 55 weight percent 3,3'-tetrathiodipropanol polysulfide mixture, about 10 to about 45 weight 35

percent of bis-(3-triethoxysilylpropyl)tetrasulfide and bis-(3-triethoxysilylpropyl)trisulfide wherein the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1; wherein the  
5 weight ratio of silica to carbon black is in a range of about 3/1 to about 30/1; wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters per gram and a dibutylphthalate (DBP) absorption value in a range of  
10 about 150 to about 300.

10. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim  
15 1.

11. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim  
20 2.

12. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim  
25 3.

13. A tire having a rubber tread wherein said  
25 tread is comprised of the rubber composition of claim 4.

14. A tire having a rubber tread wherein said  
30 tread is comprised of the rubber composition of claim 5.

15. A tire having a rubber tread wherein said  
35 tread is comprised of the rubber composition of claim 6.

16. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 7.

5           17. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 8.

10           18. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 9.

**Smart & Biggar  
Ottawa, Canada  
Patent Agents**